

Japanese Patent Office (JP)

**UNEXAMINED PATENT PUBLICATION(A)**

(11) Unexamined Patent Publication No.: 09-024667

(43) Date of Publication: January 28, 1997

(51) Int. Cl.: B41M 5/26

Examination not requested

Number of Claims: 1 OL (total 10 pages)

(21) Patent Application  
No.: 1995-176155

(22) Filing Date:  
July 12, 1995

(71) Applicant: 000122298  
Oji Paper Co., Ltd.  
4-7-5, Ginza, Chuo-ku, Tokyo,  
Japan

(72) Inventor: Syuji SAITO  
c/o Tokyo Shohin Kenkyusho of New  
Oji Paper Co., Ltd., 1-10-6,  
Shinonome, Koto-ku, Tokyo, Japan

(72) Inventor: Masahiro KAMIYA  
c/o Tokyo Shohin Kenkyusho of New  
Oji Paper Co., Ltd., 1-10-6,  
Shinonome, Koto-ku, Tokyo, Japan

(54) [Title of the invention]  
HEAT-SENSITIVE RECORDING SHEET

(57) [Abstract]

[Object] To provide a heat-sensitive recording sheet which is excellent in image quality, glossiness and image clarity as well as in recording characteristics.

[Method for achieving the object] A heat-sensitive recording sheet comprising a substrate, a heat-sensitive coloring layer provided on at least one side of the substrate, an intermediate layer optionally provided on the heat-sensitive coloring layer, and a gloss layer formed on the heat-sensitive coloring layer or the intermediate layer, the gloss layer being composed of an outer coating layer containing as main components a white pigment, a resin and a lubricant and an inner coating layer containing as a resin component an unsaturated organic compound curable by irradiation with an electron beam, the outer coating layer being formed by being released from a shaping surface with high smoothness, characterized in that the outer coating layer comprises a polyurethane and/or urethane acrylate oligomer which forms a resin film with a breaking elongation of 100 to 1,000% at a temperature of 20°C.

[Effects of the invention] The heat-sensitive recording sheet of the present invention is excellent in image quality, glossiness and image clarity as well as in recording characteristics.

[Claims]

[Claim 1] A heat-sensitive recording sheet comprising a substrate, a heat-sensitive coloring layer provided on at least one side of the substrate, an  
5 intermediate layer optionally provided on the heat-sensitive coloring layer, and a gloss layer formed on the heat-sensitive coloring layer or the intermediate layer, the gloss layer being composed of an outer coating layer containing as main components a white pigment, a resin and  
10 a lubricant and an inner coating layer containing as a resin component an unsaturated organic compound curable by irradiation with an electron beam, the outer coating layer being formed by being released from a shaping surface with high smoothness, characterized in that the outer coating  
15 layer comprises a polyurethane and/or urethane acrylate oligomer which forms a resin film with a breaking elongation of 100 to 1,000% at a temperature of 20°C.

[Detailed Description of the Invention]

[0001]

20 [Technical Field to Which the Invention Pertains]

The present invention relates to a heat-sensitive recording sheet, more specifically to a heat-sensitive recording sheet which provides recorded images that are excellent in image quality, glossiness and image  
25 clarity, as well as excellent recording characteristics.

[0002]

[Prior Art]

Heat-sensitive recording sheets generally  
comprise a support made of paper, synthetic paper, plastic  
5 film or the like, and a heat-sensitive coloring layer  
formed on one side of the support and containing as main  
constituents a colorless or pale-colored coloring  
substance such as electron-donating leuco dye, an organic  
acidic developer such as an electron-accepting phenol  
10 compound, and a binder. The color-forming dye is reacted  
with the developer upon application of thermal energy to  
thereby form a colored recorded image. Such recording  
sheets have advantages in that recording devices used  
therefor are compact, inexpensive and easy to maintain,  
15 and thus are in extensive use not only as recording media  
for facsimile machines, ticket-vending machines,  
scientific measuring instruments and so on, but also as  
output media in printers or plotters for POS labels, CAD,  
CRT medical images or the like.

20 [0003]

Among them, for use in image printers in CRT  
medical measuring instruments which require uniformity and  
high resolution in recorded images and for use in CAD  
plotters which require dimensional stability and fine-line  
25 recording, synthetic paper of multi-layer structure and

biaxially oriented thermoplastic resin films optionally containing an inorganic pigment are used. For high value-added heat-sensitive recording sheets, such as video printer paper, not only high image quality, but also enhanced glossiness and image clarity are demanded. However, in order to achieve enhanced glossiness and image clarity as well as excellent quality in recorded images, such as high uniformity and resolution, it is necessary to improve the texture and cushioning characteristics of the substrate and additionally to impart high smoothness to the outermost layer of the heat-sensitive recording sheet.

[0004]

One known method disclosed in Japanese Unexamined Patent Publication No. 1987-279980 is to use a coating composition that is curable with an ultra-violet beam or an electron beam in order to impart high smoothness to the outermost layer of a heat-sensitive recording sheet. While this method gave high glossiness, it generated rippling on the surface due to shrinking during curing, thus interfering with image clarity, and resulting in unsatisfactory quality. The present inventors conducted extensive research to overcome the above-noted problem and filed Japanese Unexamined Patent Publication No. 1995-327940 based on the finding that a gloss layer which is absolutely free of rippling due to

shrinking during curing can be produced either by applying  
onto a substrate heat-sensitive coloring layer, or onto an  
intermediate layer when such an intermediate layer is  
provided on the heat-sensitive coloring layer, a coating  
5 composition comprising as the main component an  
unsaturated organic compound curable by irradiation with  
an electron beam, bringing the resulting coating into  
close contact with a shaping surface having high  
smoothness, curing the coating with an electron beam, and  
10 then releasing the resulting layer from the shaping  
surface to thereby transfer the high smoothness of the  
shaping surface to the gloss layer cured by the electron  
beam; or by applying the coating composition onto the  
shaping surface, laminating the resulting coating with a  
15 substrate heat-sensitive coloring layer, or with an  
intermediate layer when such an intermediate layer is  
provided on the heat-sensitive coloring layer, curing the  
coating with an electron beam, and then releasing the  
resulting layer from the shaping surface to thereby  
20 transfer the high smoothness of the shaping surface to the  
gloss layer cured by the electron beam. The above  
processes enabled the production of a heat-sensitive  
recording sheet with excellent glossiness and image  
clarity.

However, there were technical problems arising from the above attempt, that is, the high smoothness imparted to the outermost layer of the heat-sensitive recording sheet increases the contact area between a thermal recording head and the outermost layer, so that the thermal recording head leaves its running trace on the outermost layer or grinds the outermost layer, producing grinding debris which will adhere to the thermal recording head, thereby greatly obstructing proper recording and, additionally, the increased likelihood of the head becoming adhered to the outermost layer under high humidity conditions leads to improper advance of the recording sheet. Hence, the quality of the obtained heat-sensitive recording sheet was not of a satisfactory level.

[0006]

As a solution to the foregoing problem, the present inventors proposed, in Japanese Unexamined Patent Publication No. 1995-125430, a method wherein a gloss layer is composed of an outer coating layer comprising a specific amount of a white pigment and an unsaturated organic compound curable by irradiation with an electron beam and an inner coating layer mainly comprising an unsaturated organic compound curable by irradiation with an electron beam, and wherein the outer coating layer is formed by being released from a shaping surface having

high smoothness. While this method realized enhanced hardness and toughness of the cured coating film by containing in the outer coating layer a specific amount of the white pigment and unsaturated organic compound curable  
5 by irradiation with an electron beam as described above, the method was still unsatisfactory in terms of avoiding recording problems and improper advance of the recording sheet under lower humidity conditions (at a temperature of 25°C and RH of 20% or lower), thus remained to be improved.

10 [0007]

[Problems to Be Solved by the Invention]

An object of the present invention is to solve the aforementioned problems associated with the prior art heat-sensitive recording sheets and provide a heat-  
15 sensitive recording sheet which is excellent in glossiness and image clarity as well as in image quality and recording characteristics under various environmental conditions ranging from low humidity to high humidity.

[0008]

20 [Means for Solving the Problems]

The present inventors conducted intensive research to achieve the above object and, as a result, developed the present invention. The present invention provides a heat-sensitive recording sheet comprising a  
25 substrate, a heat-sensitive coloring layer provided on at

least one side of the substrate, an intermediate layer optionally provided on the heat-sensitive coloring layer, and a gloss layer formed on the heat-sensitive coloring layer or the intermediate layer, the gloss layer being  
5 composed of an outer coating layer containing as main components a white pigment, a resin and a lubricant and an inner coating layer containing as a resin component an unsaturated organic compound curable by irradiation with an electron beam, the outer coating layer being formed by  
10 being released from a shaping surface with high smoothness, characterized in that the outer coating layer comprises a polyurethane and/or urethane acrylate oligomer which forms a resin film with a breaking elongation of 100 to 1,000% at a temperature of 20°C.

15 [0009]

[Modes for Carrying Out the Invention]

Examples of the substrate to be used in the present invention include synthetic paper prepared by heating and kneading a polyolefin resin and a white  
20 inorganic pigment, extruding the melt from a die, stretching the extrudate in the longitudinal direction, laminating one or two layers of a film formed from a polyolefin resin and a white inorganic pigment on both sides of the longitudinally stretched film, and stretching  
25 the obtained laminated film in the transverse direction to



make the film translucent or opaque. Further examples include a film formed by heating and kneading polyethylene, polypropylene, an ethylene-vinyl acetate copolymer resin, polyvinyl chloride, polystyrene, polyester or like thermoplastic resin either singly or in combination, extruding the melt from a die and biaxially stretching the extrudate; an opaque film formed from a mixture of the above-exemplified resin and a white inorganic pigment by biaxial stretching; and a paper made of pulp fibers such as wood-free paper, mechanical paper, roll paper, recycled paper, coated paper and the like. A support made of pulp fibers, when used, is preferably provided thereon with a coating layer before being provided with a heat-sensitive layer in order to improve the uniformity of the images.

[0010]

The heat-sensitive coloring layer according to the present invention can be formed by applying a heat-sensitive coloring layer coating composition which mainly comprises a colorless or pale-colored electron-donating leuco dye, an organic acidic substance that causes the leuco dye to develop a color by application of heat, and a binder, and which optionally comprises a cross-linking agent, a pigment, or a heat-fusible substance. It is generally preferred, from the viewpoint of coloring sensitivity and color density, that the coating amount of

the heat-sensitive coloring layer be 3 to 15 g/m<sup>2</sup>. The coating may be performed using a technique generally employed by those skilled in the art, such as air knife coating, Meyer bar coating, blade coating, reverse roll coating or slit die coating. The surface of the heat-sensitive coloring layer may be subjected to a smoothing treatment, for example, with a super calender, gloss calender, machine calender or the like, in order to improve the coatability and thereby enhance the recording density and sensitivity.

[0011]

As the color-forming dye, a colorless or pale-colored electron-donating leuco dye that reacts with the developer upon heating to develop a color is used. The color-forming dye usable in the present invention includes, for example, at least one member selected from the group consisting of 2,2 bis{4-[6'-(N-cyclohexyl-N-methylamino)-3'-methylspiro(phthalide-3,9'-xanthene)-2'-ylamide]phenyl}propane, 3-diethylamino-6-methyl-7-anilino-fluoran, 3-piperidino-6-methyl-7-anilino-fluoran, 3-(N-methyl-N-cyclohexyl)amino-6-methyl-7-anilino-fluoran, 3-dimethylamino-7-chloroanilino-fluoran, 3-[N-ethyl-N-(p-methylphenyl)amino]-6-methyl-7-anilino-fluoran, 3-diethylamino-7-(metatrifluoromethyl)anilino-fluoran, 3-(N-ethyl-N-tetrahydrofurfuryl)amino-6-methyl-7-

anilinofluoran, 3-(N-ethyl-N-isopentyl)amino-6-methyl-7-anilinofluoran, 3-(N,N dibutyl)amino-6-methyl-7-anilinofluoran and like fluoran-based dyes.

[0012]

5           The developer used in the present invention comprises an electron-accepting organic acidic substance that reacts with the color-forming dye upon heating to thereby develop a color. The developer is liquefied or evaporated at room temperature or higher, preferably 70°C  
10 or higher, so that it can react with the color-forming dye, thereby causing the dye to develop a color. The developer is generally used in an amount of 1 to 5 weight parts, preferably 1.5 to 3 weight parts, per weight part of the color-forming dye in order to maximize the color density.

15           [0013]

          The developer includes, for example, at least one member selected from the group consisting of 4,4'-isopropylidenediphenol(bisphenol A), 4,4'-isopropylidenebis(2-chlorophenol), 4,4'-  
20 isopropylidenebis(2-methylphenol), 4,4'-isopropylidenebis(2,6-t-butylphenol), 4,4'-sec-butylidenediphenol, 4,4'-cyclohexylidenediphenol, 4-t-butylphenol, 4-phenylphenol, 4-hydroxydiphenoxide, 4,4'-dihydroxydiphenylsulfone, 2,4'-dihydroxydiphenylsulfone,  
25 3,3'-dihydroxydiphenylsulfone, 3,3'-diamino-4,4'-

dihydroxydiphenylsulfone, 3,3'-diallyl-4,4'-  
dihydroxydiphenylsulfone, 3,3'-dichloro-4,4'-  
dihydroxydiphenylsulfone, 4-hydroxydiphenylsulfone, 4-  
hydroxy-4'-isopropoxydiphenylsulfone, 4-hydroxy-4'-  
5 benzyloxydiphenylsulfone, 2,4-dihydroxydiphenylsulfone,  
2,4-dihydroxy-4'-methyldiphenylsulfone and 3,4-  
dihydroxyphenyl-p-tolylsulfone.

[0014]

According to the present invention, the heat-  
10 sensitive coloring layer may contain either a water-  
soluble resin or a water-dispersible resin as the binder.  
Examples are water-soluble resins such as polyvinyl  
alcohol, starch, modified starch, gum arabic, gelatin,  
casein, chitosan, methyl cellulose, hydroxy methycellulose,  
15 hydroxy ethylcellulose, polyvinyl pyrrolidone, polyacrylic  
acid salt, polyacrylamide, polyester resins, styrene-  
acrylate copolymer resins, styrene-maleic anhydride  
copolymer resins, methylvinylether-maleic anhydride  
copolymer resins and isopropylene-maleic anhydride  
20 copolymer resins, and water-dispersible resins such as  
vinyl acetate emulsion, acrylate copolymer emulsion,  
methacrylate copolymer emulsion, polyurethane emulsion,  
polyvinyl chloride emulsion, SBR latex, MBR latex and like  
emulsions having a good film-forming ability, i.e., a  
25 minimum film-forming temperature of 20°C or lower. These

resins can be used singly or in combination.

[0015]

It is, however, important to assure that the mixture, which is obtained by mixing the binder with a dispersion of each of the color-forming dye and the developer, does not develop a color, coagulate or exhibit high viscosity, and that the formed heat-sensitive recording layer film is tough and free from desensitization. Preferably, the binder is contained in the heat-sensitive coloring layer in an amount of 8 to 25% by weight based on the weight of the solids of the heat-sensitive coloring layer. An amount of less than 8% by weight decreases the strength of the coating film, while an amount of more than 25% by weight deteriorates the sensitivity.

[0016]

The heat-sensitive coloring layer may also contain a cross-linking agent for curing resins for the purpose of increasing its water resistance. Examples of the cross-linking agent include glyoxal, dialdehyde starch and like dialdehyde compounds, polyethyleneimine and like polyamine compounds, epoxy compounds, polyamide resins, melamine resins, glyceringlycidylether and like diglycidyl compounds, dimethylolurea compounds, aziridine compounds, block isocyanate compounds, ammonium persulfate, ferric

chloride, magnesium chloride, sodium tetraborate,  
potassium tetraborate and like inorganic compounds, boric  
acid, boric acid triesters, boron-based polymers, etc.  
The cross-linking agent may be used in an amount of 1 to  
5 10% by weight based on the weight of the solids of the  
heat-sensitive coloring layer.

[0017]

The heat-sensitive coloring layer may further  
contain, in order to increase its whiteness and improve  
10 the uniformity of the images, a finely powdered pigment  
which has high whiteness and an average particle size of 5  
 $\mu\text{m}$  or smaller. Examples of such pigments include  
inorganic pigments such as calcium carbonate, magnesium  
carbonate, kaolin, clay, talc, calcined clay, silica,  
15 diatomaceous earth, synthetic aluminum silicate, zinc  
oxide, titanium oxide, aluminum hydroxide, barium sulfate  
and surface-treated calcium carbonate and silica; and  
organic pigments such as urea-formalin resins, styrene-  
methacrylic acid copolymer resins and polystyrene resins.  
20 Preferably, the pigment is contained in an amount of 40%  
by weight or less based on the weight of the solids of the  
heat-sensitive coloring layer so as to prevent a reduction  
in color density.

[0018]

25 Examples of usable heat-fusible substances

include stearic acid amide, stearic acid bisamide,  
oleamide, palmitic acid amide, cocamide, behenamide and  
like fatty acid amides, zinc stearate, calcium stearate,  
polyethylene wax, carnauba wax, paraffin wax, ester wax  
5 and like waxes, dimethyl terephthalate, dibutyl  
terephthalate, dibenzyl terephthalate, dibutyl  
isophthalate, phenyl 1-hydroxynaphthoate, 1,2-di(3-  
methylphenoxy)ethane, 1,2 diphenoxyethane, 1-phenoxy-2-(4-  
methylphenoxy)ethane, diphenyl carbonate, p-benzylbiphenyl,  
10 2,2'-methylenebis(4-methyl-6-t-butylphenol), 4,4'-  
butylidenebis(6-t-butyl-3-methylphenol), 1,1,3 tris(2-  
methyl-4-hydroxy-5-t-butylphenyl)butane, 2,2'-  
methylenebis(4-ethyl-6-t-butylphenol),  
2,4-di-t-butyl-3-methylphenol, 4,4'-thiobis(3-methyl-6-t-  
15 butylphenol) and like hindered phenols, 2-(2'-hydroxy-5'-  
methylphenyl)-benzotriazole, 2-hydroxy-4-  
benzyloxybenzophenone and like sensitizers, antioxidants  
and UV absorbers.

[0019]

20 Generally, it is preferred that the heat-fusible  
substance be contained in the heat-sensitive coloring  
layer in an amount of 4 weight parts or less per weight  
part of the developer. For the purpose of improving the  
wetting property of the heat-sensitive coloring layer  
25 coating composition and preventing fish eyes in the

coating, it is possible to further add a wetting property improver such as acetylene glycol or dialkyl sulfosuccinate, a dispersing agent for pigment, a defoaming agent, a fluorescent dye, a coloring pigment and  
5 the like.

[0020]

In the heat-sensitive recording sheet of the present invention, it is effective to provide an intermediate layer between the heat-sensitive coloring  
10 layer and the gloss layer from the standpoint of ensuring adhesion between the heat-sensitive coloring layer and the gloss layer, preventing the fogging which is apt to occur during the application or curing of the gloss layer, etc. The intermediate layer can be formed by applying, onto the  
15 heat-sensitive coloring layer, a coating composition comprising as main constituents a water-soluble and/or a water-dispersible resin, a pigment, a cross-linking agent and a lubricant such that the coating amount after drying is 1.0 to 10.0 g/m<sup>2</sup>. A coating amount of less than 1.0  
20 g/m<sup>2</sup> results in a coating film unevenly formed and having pinholes and defects, thus leading to degraded image quality and surface characteristics. On the other hand, a coating amount exceeding 10.0 g/m<sup>2</sup> results in decreased sensitivity and therefore lowered recording density. The  
25 coating may be performed by the same method as that



employed for the formation of the heat-sensitive coloring layer.

[0021]

In order to facilitate the formation of the  
5 gloss layer and to thereby improve the recording density,  
sensitivity and glossiness, the surface of the  
intermediate layer may be subjected to a smoothing  
treatment with a super calender, gloss calender, machine  
calender or the like. The amount of the resin to be  
10 contained in the intermediate layer is preferably 20 to  
80% by weight based on the weight of the solids of the  
intermediate layer. The amount of the pigment to be  
contained in the intermediate layer is 20 to 80% by weight  
based on the weight of the solids of the intermediate  
15 layer. If the resin is contained in an amount of more  
than 80% by weight, sticking may be caused during  
recording. If the resin is contained in an amount of less  
than 20% by weight, the barrier property of the coating  
film is degraded, thereby causing fogging and,  
20 additionally, the ability to prevent penetration of the  
inner coating layer coating composition is decreased,  
ultimately failing to strengthen the adhesion between the  
heat-sensitive coloring layer and the gloss layer.  
Preferably, the cross-linking agent is used in an amount  
25 of 30% by weight or less based on the weight of the solids

of the intermediate layer. The resin, pigment and cross-linking agent to be used in the intermediate layer can be suitably selected from those used for the heat-sensitive coloring layer.

5 [0022]

Examples of the lubricant to be used in the intermediate layer of the invention include zinc stearate, calcium stearate, polyethylene wax, carnauba wax, paraffin wax, ester wax and like waxes, lauryl phosphate, oleyl  
10 phosphate, stearyl phosphate and like alkyl phosphates and alkali metal salts or amine salts, lauryl sulfonate, oleyl sulfonate, stearyl sulfonate and like alkyl sulfonates and alkali metal salts or amine salts, glyceryl monomyristate, glyceryl monostearate, glyceryl monooleate, glyceryl  
15 distearate, glyceryl dioleate and like glycerine fatty acid esters, diglyceryl monolaurate, diglyceryl dilaurate, tetraglyceryl monolaurate, hexaglyceryl monolaurate, decaglyceryl monolaurate and like polyglycerine fatty acid esters, dimethylpolysiloxane, and their modified products.  
20 Selection should be made from those which do not cause desensitization, decoloring or fogging. It is preferred that the lubricant be contained in an amount of 10% by weight or less based on the weight of the solids of the intermediate layer.

25 [0023]

The inner coating layer, which forms a part of the gloss layer of the invention, can be formed by applying a coating composition comprising as a resin component an unsaturated organic compound curable by irradiation with an electron beam such that the coating amount after drying is 1.0 to 10.0 g/m<sup>2</sup>. If the coating amount is more than 10.0 g/m<sup>2</sup>, the sensitivity is deteriorated and, even with the help of an increased coating amount of the heat-sensitive coloring layer, the recording density is decreased. If the coating amount is less than 1.0 g/m<sup>2</sup>, the outer coating layer containing a large amount of white pigment cannot be satisfactorily released from the shaping surface and, further, the adhesion of the inner coating layer to the heat-sensitive coloring layer or the intermediate layer is not sufficient.

[0024]

Examples of the electron beam-curable unsaturated organic compound to be used in the inner coating layer forming a part of the gloss layer of the invention include acrylate or methacrylate monomers and oligomers having at least one ethylenically unsaturated bond.

[0025]

Monomers having at least one ethylenically unsaturated bond for use in the invention are not limited.

Examples of monofunctional monomers include N-vinylpyrrolidone, acrylonitrile or derivatives thereof, styrene or derivatives thereof, acrylamide and like amide group-containing monomers; benzyl acrylate, 2-ethylhexyl  
5 acrylate, 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, tetrahydrofurfuryl acrylate, phenoxyethyl acrylate, nonylphenoxyethyl acrylate, acrylates of  $\epsilon$ -caprolactone adducts, butoxyethyl (meth)acrylate, 2-hydroxy-3-phenoxypropyl acrylate, cyclohexyl  
10 (meth)acrylate, N,N-dimethylamino (meth)acrylate, N,N-dimethylaminoethyl (meth)acrylate, 3-phenoxypropyl acrylate, 2-methoxyethyl (meth)acrylate and like acrylates or methacrylates. Examples of monomers having two or more ethylenically unsaturated bonds include hexanediol  
15 diacrylate, neopentyl glycol diacrylate, diethylene glycol diacrylate, tripropylene glycol diacrylate, tetraethylene glycol diacrylate, tricyclodecane-dimethylol diacrylate, trimethylolpropane triacrylate, ditrimethylolpropane tetraacrylate, diacrylate of ethylene oxide-modified  
20 bisphenol A and the like.

[0026]

Other examples of compounds that can serve as lubricants include stearyl-modified pentaerythritol diacrylate, lauryl (meth)acrylate and like fatty acid-  
25 modified acrylates or methacrylates, silicone-modified

(meth)acrylates, fluorine-modified (meth)acrylates, etc. These compounds, having at least one ethylenically unsaturated bond, can be used either singly or in a combination of two or more species as required.

5 [0027]

Examples of acrylate or methacrylate oligomers having at least one ethylenically unsaturated bond include, for example, urethane acrylate oligomers, polyester acrylate oligomers and butadiene-modified acrylate  
10 oligomers. These oligomers can be used singly or in a combination of two or more species.

[0028]

In order to obtain the hardness desired for the coating film, it is particularly preferred to use  
15 polyfunctional compounds which have at least three functional groups and which can provide high crosslinkability. Examples of such polyfunctional compounds include acrylate of caprolactone-modified dipentaerythritol, ethylene oxide-modified  
20 trimethylolpropane triacrylate, dipentaerythritol hexa(penta)acrylate and the like.

[0029]

If desired, the inner coating layer, which forms a part of the gloss layer of the invention, may further  
25 contain a white pigment, a lubricant, etc., suitably

selected from those used for the intermediate layer. If  
necessary, a non-reactive lubricant having no  
ethylenically unsaturated bond may also be used, insofar  
as it does not impair the desired curability as in the  
5 case of other non-reactive substances.

[0030]

The electron beam-curable composition according  
to the invention may incorporate a polymer that is soluble  
therein. However, the use of the polymer in an  
10 excessively large amount impairs the curability of the  
coating film and is not preferable from the standpoint of  
resistance to scratches, resistance to organic solvents,  
etc. When the coating composition, which is obtained by  
dispersing a white pigment, a lubricant or the like in the  
15 ethylenically-unsaturated-bond-containing monomer or  
oligomer described above, has high viscosity, it is  
effective that the coating composition be either diluted  
with an organic solvent, then applied and dried, or that  
it be emulsified for increased operability or diluted with  
20 water (if it is water-soluble), then applied and dried,  
and finally cured with an electron beam.

[0031]

The above white pigment, lubricant, etc., can be  
dispersed in the electron beam-curable unsaturated organic  
25 compound with the use of a three roll mill, two roll mill,

Cowles Dissolver, homomixer, sand grinder, paint conditioner, ultrasonic dispersing machine or the like. The inner coating layer coating composition can be applied using a technique generally employed by those skilled in  
5 the art, such as offset gravure coating, air knife coating, Meyer bar coating, blade coating, reverse roll coating or slit die coating.

[0032]

The outer coating layer, which forms a part of  
10 the gloss layer of the invention, is formed by applying a coating composition comprising a white pigment, a resin and a lubricant as principal components, wherein the resin is a polyurethane and/or urethane acrylate oligomer. It is preferred that the property of the dried coating film  
15 be such that the breaking elongation at a temperature of 20°C falls within the range of 100% to 1,000%. The coating composition is applied in such a manner that the coating amount after drying is 1.0 to 10.0 g/m<sup>2</sup>. A breaking elongation smaller than 100% causes recording  
20 problems due to the grinding debris adhered to the thermal recording head, thus not favorable. A breaking elongation larger than 1,000% improves the wear resistance against the thermal recording head, however, it results in insufficient hardness of the coating film even if the  
25 pigment is added, leading to improper advance of the

recording sheet, and thus not also favorable. In addition,  
if the coating amount is more than  $10.0 \text{ g/m}^2$ , the  
sensitivity is decreased and, even with the help of an  
increased coating amount of the heat-sensitive coloring  
5 layer, the recording density is decreased. If the coating  
amount is less than  $1.0 \text{ g/m}^2$ , the releasability from the  
shaping surface is degraded and, further, high image  
clarity and glossiness are not likely to be achieved.

[0033]

10 Preferably, the white pigment is contained in an  
amount as large as possible from the standpoint of  
enhancing the hardness of the coating film. More  
preferably, the proportion of the white pigment is  
selected such that the weight ratio (A/B) of the white  
15 pigment (A) to the resin (B) is within the range of 40/60  
to 95/5. A weight ratio A/B of more than 95/5 results in  
failing to achieve high releasability from the shaping  
surface and excellent surface characteristics of the  
coating film, whereas an weight ratio A/B of less than  
20 40/60 results in failing to give the desired hardness.

[0034]

According to the present invention, in addition  
to the above-described resin, other resins can also be  
contained in the outer coating layer, insofar as they do  
25 not deteriorate the desired effect of the invention.



Although it is preferred that the lubricant be contained in a large amount for effective prevention of improper advance of the recording sheet, the desired hardness would not be achieved if the lubricant is added in an amount  
5 exceeding 10 weight parts per 100 weight parts of the sum of A and B. The pigment, resin, and lubricant to be used in the outer coating layer can be suitably selected from the variety of those used for the intermediate layer or the inner coating layer.

10 [0035]

Electron-beam accelerators for use in electron beam irradiation are not limited and include, for example, electro-curtain type, scanning type and like electron beam irradiators. Among them, those of electro-curtain type  
15 which are inexpensive and capable of obtaining high output can be effectively used. An electron beam is irradiated at an accelerating voltage of preferably 100 kV or higher. In order to minimize the damage to the substrate, it is preferred that the curing be successfully accomplished  
20 with a minimum absorption dosage of the electron beam.

[0036]

The highly smooth shaping surfaces which can be used for the present invention are those having dimensional stability, such as, metal drums, metal rolls,  
25 metal films and plastic films. It is required that the

surface be highly polished into a specular gloss. If required, a mold release agent can be applied to the shaping surface to facilitate easy separation of the surface. Examples of usable mold release agents include  
5 zinc stearate, calcium stearate and like higher fatty acid-based mold release agents, polyethylene wax and like waxes, silicone compounds and like mold release agents, etc.

[0037]

10           The outer coating layer and the inner coating layer are brought into close contact with each other to thereby form a gloss layer of the invention, and then cured and unified by irradiation with an electron beam in accordance with either of the following two methods. One  
15 method comprises bringing the outer coating layer provided on the highly smooth shaping surface into close contact with the inner coating layer provided on the heat-sensitive coloring layer or the intermediate layer, and irradiating the resulting laminate with an electron beam  
20 from the opposite side of the heat-sensitive recording sheet or from the shaping surface side. The other method comprises directly applying the inner coating layer coating composition onto the outer coating layer provided on the highly smooth shaping surface, bringing the  
25 obtained layer into close contact with the heat-sensitive

coloring layer or the intermediate layer, and irradiating the resulting laminate with an electron beam from the opposite side of the heat-sensitive recording sheet or from the shaping surface side. The latter method may be performed in a similar way to that of the former method if the inner coating layer coating composition is high in viscosity and therefore less likely to penetrate into the outer coating layer coating composition.

[0038]

The surface of the gloss layer formed as described above exhibits high smoothness, excellent glossiness and image clarity. Specifically, it is preferred that the glossiness be 80% or higher when measured at an angle of 75 degrees in accordance with JIS-Z-8714, and that the image clarity be 80% or higher, preferably 90%, when converted from the value of distinctness of image measured at an optical comb width of 2 mm in accordance with JIS-K-7105.

[0039]

[EXAMPLES]

The present invention will be described below in further detail with reference to the following examples to which, however, the invention is not limited. The parts and percentages used in the examples are all by weight unless otherwise specified.

Example 1

A heat-sensitive coloring layer coating composition obtained as described later was applied to one surface of commercially available synthetic paper (trade name "YUPO FPG-80", product of YUPO Corporation) in an amount of 5.5 g/m<sup>2</sup> on a dry weight basis by a bar coating method, and thereon was applied an intermediate layer coating composition in an amount of 1.5 g/m<sup>2</sup> on a dry weight basis. To the resultant intermediate layer, an inner coating layer coating composition for gloss layer was applied in an amount of 3.0 g/m<sup>2</sup>, thereby forming an inner coating layer. Aside from the above, an outer coating layer coating composition was applied to a 75-μm-wide PET film (trade name "Lumirror T", product of TORAY Industries, Inc.) in an amount of 3.0 g/m<sup>2</sup> on a dry weight basis, thereby forming an outer coating layer. Subsequently, the outer coating layer was brought into close contact with the inner coating layer to form a gloss layer composed of the outer coating layer and the inner coating layer, which was then cured by irradiation with an electron beam from the PET film side at an absorbed dose of 3.0 Mrads and an accelerating voltage of 175 kV with an electron-curtain type electron beam accelerator (product of Energy Sciences, Inc.), thereby completely unifying the outer coating layer with the inner coating layer.

Thereafter, the PET film was peeled off from the gloss layer, whereby a heat sensitive recording sheet was obtained.

[0040]

- 5 • Preparation of heat-sensitive coloring layer coating composition

Dispersion A (heat-sensitive color-forming dye dispersion)

	3-(N,N-dibutyl)amino-6-methyl-7-anilinofluoran	20 parts
10	10% aqueous solution of polyvinyl alcohol	20 parts
	Water	10 parts

Dispersion B (developer dispersion)

	4-hydroxy-4'-isopropoxydiphenylsulfone	50 parts
	10% aqueous solution of polyvinyl alcohol	50 parts
15	Water	25 parts

Each of Dispersions A and B were separately dispersed and pulverized to an average particle size of  $1.0 \pm 0.3 \mu\text{m}$  with an Ultra Visco Mill. Thereafter, 30 parts of Dispersion A, 90 parts of Dispersion B, 52 parts of a 20 60% slurry of calcium carbonate, 40 parts of a 10% aqueous solution of polyvinyl alcohol, 28 parts of a SBR latex (trade name "L-1537", solid conc. 50%, product of Asahi Chemical Industry Co., Ltd.), 11 parts of stearic acid amide (trade name "Cerozol A-877", solid conc. 26.5%, 25 product of Chukyo Yushi Co., Ltd.) and 82 parts of water

were mixed to thereby obtain a heat-sensitive coloring layer coating composition.

[0041]

- Intermediate layer coating composition (solid conc. 15%)

5                   An intermediate layer coating composition was prepared by mixing the following:

	60% dispersion of kaolinitic clay (with an average particle size of 0.6 $\mu$ m)	42 parts
	Aqueous solution of carboxylic acid-	
10	modified polyvinyl alcohol (solid conc. 10%) (trade name "Gohsenal T-330", product of The Nippon Synthetic Chemical Industry Co., Ltd.)	200 parts
	Acrylic emulsion	
15	(trade name "SC-2250", solid conc. 40%, product of Nippon Shokubai Co., Ltd.)	100 parts
	Solution of dimethylolurea (trade name "J-001", solid conc. 30%, product of Showa Denko K.K.)	33 parts
20	40% dispersion of zinc stearate (with an average particle size of 0.9 $\mu$ m) (trade name "Hymicron F-930", product of Chukyo Yushi Co., Ltd.)	13 parts
	Water	279 parts

25                   [0042]

• Outer coating layer coating composition for gloss layer

An outer coating layer coating composition for gloss layer was prepared by mixing the following:

	No. 1 fraction kaolin (trade name "UW-90",	
5	product of Engelhard Corporation)	65 parts
	Polyurethane emulsion	
	(trade name "UE-1101", solid conc. 35%,	
	product of Toagosei Co., Ltd.)	92 parts
	Potassium stearyl phosphate	
10	(trade name "Upol 1800", solid conc. 35 %,	
	product of Matsumoto Yushi-Seiyaku Co., Ltd.)	8 parts
	Water	35 parts

[0043]

• Inner coating layer coating composition for gloss layer

15           An inner coating layer coating composition for gloss layer was prepared by mixing the following:

	Acrylate of caprolactone-modified	
	dipentaerythritol	
	(trade name "KAYARAD DPCA-60",	
20	product of Nippon Kayaku Co., Ltd.)	70 parts
	Epichlorohydrin-modified propylene	
	glycol diacrylate	
	(trade name "Denacol DA-911,	
	product of Nagase Chemtex Corporation)	30 parts

25           In addition, before forming a gloss layer, a

back layer coating composition was applied to the opposite side of the substrate in an amount of 1.5 g/m<sup>2</sup> on a dry weight basis by a bar coating method, after which the obtained coating was subjected to a smoothing treatment with a super calender.

[0044]

• Back layer coating composition

A back layer coating composition was prepared by mixing the following:

10	Sodium polystyrene sulfonate (trade name "CHEMISTAT SA-9", solid conc. 33%, product of Sanyo Chemical Industries, Ltd.) SBR latex	30 parts
15	(trade name "0528", solid conc. 50%, product of JSR Corporation) 10% aqueous solution of oxidized starch (trade name "ACE A", product of Oji Cornstarch Co., Ltd.)	70 parts 150 parts
20	60% slurry of kaolinitic clay Water	67 parts 83 parts

[0045]

Aside from the above, the above-described outer coating layer coating composition for gloss layer was applied to one surface of a 75- $\mu$ m-wide PET film in an



amount of 40 g/m<sup>2</sup> on a dry weight basis by using a wire bar, and then dried for 15 minutes at a temperature of 80°C. Subsequently, the obtained resin film was peeled off from the PET film, whereby a specimen for tension test  
5 was obtained. Further, the film obtained after the application of the electron beam-curable unsaturated organic compound was dried by irradiation with an electron beam at an absorbed dose of 3.0 Mrads and an accelerating voltage of 175 kV.

10 [0046]

#### Example 2

The procedure of Example 1 was repeated except that the outer coating layer coating composition for gloss layer was replaced with the one prepared by mixing the  
15 following:

No. 1 fraction kaolin (trade name "UW-90", product of Engelhard Corporation)	65 parts
Urethane acrylate emulsion (trade name "WE-101", solid conc. 40%, 20 product of Dai-ichi Kogyo Seiyaku Co., Ltd.)	80 parts
Potassium stearyl phosphate (trade name "Upol 1800", solid conc. 35 %, product of Matsumoto Yushi-Seiyaku Co., Ltd.)	8 parts
Water	47 parts

25 [0047]

Example 3

The procedure of Example 1 was repeated except that the outer coating layer coating composition for gloss layer was replaced with the one prepared by mixing the

5 following:

Calcium carbonate

(trade name "Raiton A",

product of Bihokufunka Kogyo K.K.) 62 parts

Urethane acrylate oligomer

10 (trade name "DIABEAM UK-6039",

product of Mitsubishi Rayon Co., Ltd.) 35 parts

Polysiloxane

(trade name "PERENOL S43", solid conc. 30%,

product of San Nopco Limited) 10 parts

15 Toluene 93 parts

[0048]

Example 4

The procedure of Example 1 was repeated except that the outer coating layer coating composition for gloss  
20 layer was replaced with the one prepared by mixing the following:

No. 1 fraction kaolin (trade name "UW-90",

product of Engelhard Corporation) 65 parts

Polyurethane emulsion

25 (trade name "UE-1101", solid conc. 35%,

- product of Toagosei Co., Ltd.) 46 parts
- Urethane acrylate emulsion
- (trade name "WE-101", solid conc. 40%,
- product of Dai-ichi Kogyo Seiyaku Co., Ltd.) 40 parts
- 5 Potassium stearyl phosphate
- (trade name "Upol 1800", solid conc. 35 %,
- product of Matsumoto Yushi-Seiyaku Co., Ltd.) 8 parts
- Water 40 parts

[0049]

10 Comparative Example 1

The procedure of Example 1 was repeated except that the outer coating layer coating composition for gloss layer was replaced with the one prepared by mixing the following:

- 15 No. 1 fraction kaolin (trade name "UW-90",
- product of Engelhard Corporation), 65 parts
- Polyurethane emulsion
- (trade name "AP-40", solid conc. 23%,
- product of Dainippon Ink and Chemicals,
- 20 Incorporated) 140 parts
- Potassium stearyl phosphate
- (trade name "Upol 1800", solid conc. 35 %,
- product of Matsumoto Yushi-Seiyaku Co., Ltd.) 8 parts

The breaking elongation of this resin film was

25 15% at a temperature of 20°C.

[0050]

Comparative Example 2

The procedure of Example 1 was repeated except that the outer coating layer coating composition for gloss  
5 layer was replaced with the one prepared by mixing the following:

	No. 1 fraction kaolin (trade name "UW-90", product of Engelhard Corporation)	65 parts
	Urethane acrylate emulsion 10 (trade name "UE-7250", solid conc. 50%, product of Toagosei Co., Ltd.)	64 parts
	Potassium stearyl phosphate (trade name "Upol 1800", solid conc. 35 %, product of Matsumoto Yushi-Seiyaku Co., Ltd.)	8 parts
15	Water	63 parts

The breaking elongation of this resin film was 5% at a temperature of 20°C.

[0051]

Comparative Example 3

20 The procedure of Example 1 was repeated except that the outer coating layer coating composition for gloss layer was replaced with the one prepared by mixing the following:

	Calcium carbonate	
25	(trade name "Raiton A",	

	product of Bihokufunka Kogyo K.K.)	62 parts
	Urethane acrylate oligomer	
	(trade name "ARONIX M-1100",	
	product of Toagosei Co., Ltd.)	35 parts
5	Polysiloxane	
	(trade name "PERENOL S43", solid conc. 30%,	
	product of San Nopco Limited)	10 parts
	Toluene	93 parts

The breaking elongation of this resin film was  
10 50% at a temperature of 20°C.

[0052]

#### Comparative Example 4

The procedure of Example 1 was repeated except  
that the outer coating layer coating composition for gloss  
15 layer was replaced with the one prepared by mixing the  
following:

	No. 1 fraction kaolin (trade name "UW-90",	
	product of Engelhard Corporation)	65 parts
	Polyurethane emulsion	
20	(trade name "S-1020", solid conc. 50%,	
	product of Hodogaya Chemical Co., Ltd.)	64 parts
	Potassium stearyl phosphate	
	(trade name "Upol 1800", solid conc. 35 %,	
	product of Matsumoto Yushi-Seiyaku Co., Ltd.)	8 parts
25	Water	63 parts

The breaking elongation of this resin film was 1,050% at a temperature of 20°C.

[0053]

The heat-sensitive recording sheets obtained in Examples 1 to 4 and Comparative Examples 1 to 4, having a width of 110 mm, were moisture-conditioned for 2 hours under the environmental condition of 25°C and RH 20%, and then subjected to a recording operation using a thermal printer (available under the trade name of "UP-860", from Sony Corporation). Image quality, recording problems and improper advance of the recording sheet were checked and rated on the following criteria. Also, through a tension test, breaking elongation of each of the obtained 20-mm-wide specimens was calculated as described below.

[0054]

(1) Image quality

Each of the five recorded heat-sensitive recording sheets were visually inspected for distinctness, contrast and density irregularity in the image, and rated on the following criteria. o: Good; o~Δ: Fairly good; Δ: Neither good nor bad, Δ~x; Fairly bad; x: Bad.

(2) Recording problems

Each of the five recorded heat-sensitive recording sheets were visually inspected in terms of recording problems resulting from the running trace of the

thermal recording head or the grinding debris adhered to the same, and rated on the following criteria. o: Good; o~Δ: Fairly good; Δ: Neither good nor bad, Δ~x; Fairly bad; x: Bad.

5 (3) Improper advance of the recording sheet

Each of the five recorded heat-sensitive recording sheets were visually inspected in terms of duration of operation and recording irregularities with horizontal stripes, and rated on the following criteria.

10 o: Good; o~Δ: Fairly good; Δ: Neither good nor bad, Δ~x; Fairly bad; x: Bad.

[0055]

(4) Breaking elongation

The specimen was set to a tension test machine  
15 (available under the trade name of "STROGRAPH", from Toyo Seiki Co., Ltd.) with a gripping length of 10 mm, and then stretched at a tension speed of 5 mm/min. Breaking elongation was calculated based on the tensile stress-strain curve of the coating film. As is evident from the  
20 results shown in Table 1, the heat-sensitive recording sheets of Examples 1 to 4 showed excellent performance in both image quality and recording characteristics even under low humidity environmental conditions, whereas the heat-sensitive recording sheets of Comparative Examples 1  
25 to 4 showed in some respects lower performance than those

of Examples 1 to 4, the degrees of which varied depending on the sheet.

[Table 1]

	Glossi- ness (%)	Image clarity (%)	Image quality	Recording problems	Improper advance of the recording sheet	Breaking elongation (%)
Ex. 1	91	92	o	o	o	610
Ex. 2	93	92	o	o	o	350
Ex. 3	91	92	o	o	o	140
Ex. 4	91	94	o	o	o	200
Comp. Ex. 1	92	91	o	x	o	15
Comp. Ex. 2	91	92	o	x	o	5
Comp. Ex. 3	92	92	o	x	o	50
Comp. Ex. 4	91	91	o	o	x	1,050

5

[Effects of the Invention]

As is evident from Table 1 above, the heat-sensitive recording sheet of the present invention provides recorded images that are excellent in image quality, glossiness and image clarity, as well as excellent recording characteristics, and thus is very useful in practical applications.